

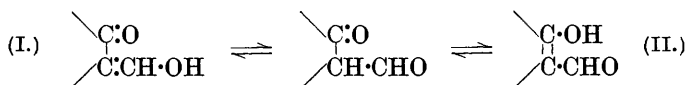
NOTES.

The Mechanism of Cyanoacetamide and Cyanoacetic Ester Condensations. A Reply. By JOGENDRA CHANDRA BARDHAN.

A SHORT time ago (J., 1929, 2225) the author discussed Ingold's view (J., 1921, 119, 330) that monoketonic compounds react with ethyl cyanoacetate in the enolic form, in the light of the contrary observations of Kohler and Corson (*J. Amer. Chem. Soc.*, 1923, 45, 1975) and of Lapworth and McRae (J., 1922, 121, 2741). In a recent communication (this vol., p. 184) Ingold states that the author's account of his work on the subject is misleading inasmuch as his subsequent modified views (J., 1926, 1868) have not been taken into consideration. In this later paper Ingold's references to aldol condensation are very brief. Indeed, no mention is made of

his earlier work or of the subsequent demonstrations of Kohler, Lapworth, and others which are definitely at variance with his hypothesis. In these circumstances the omission by the author of any reference to this paper was unavoidable.

The evidence which Ingold brings forward in support of the statement that in an enolised β -diketone carbon coupling consistently occurs at enolic carbon is not conclusive. There can be little doubt that in ethoxymethylene-ketones and other $\alpha\beta$ -unsaturated ketones, e.g., mesityl oxide, benzylideneacetone, etc., the ethylenic double bond takes part in additive reactions; but it is not clear to the author why similar considerations would hold in the case of enolised 1:3-dicarbonyl compounds where owing to prototropic changes the enolic double bond cannot always remain in the $\alpha\beta$ -position. Furthermore, Ingold assumes that in hydroxymethylenecyclohexanone the direction of enolisation is beyond doubt and carbon coupling takes place at the enolic carbon, leading to the formation of a quinoline derivative. So far as the author is aware, scarcely any work appears to have been done on the constitution of hydroxymethylenecyclohexanone. On general grounds it is, however, quite conceivable that equilibrium exists between the hydroxymethylene form (I) and the aldo-enolic form (II), especially as the cyclohexane ring exhibits a marked tendency to acquire a double bond (compare, for instance, Dieckmann, *Annalen*, 1901, **317**, 27; Birch, Kon, and Norris, J., 1923, **123**, 1368). Consequently the view that in



hydroxymethylenecyclohexanone the direction of enolisation is fixed cannot be regarded as correct. According to the author's view, the preferential formation of the quinoline derivative is explicable by the superior activity of the aldehyde group in comparison with the carbonyl. The author's observations, however, are based on only a few instances and therefore it seems desirable to postpone discussion until further experiments have been performed.

—UNIVERSITY COLLEGE OF SCIENCE, CALCUTTA. [Received, May 12th, 1930.]

The Preparation of Anhydrous Oxalic Acid. By ERIC IAN JOHNSON and JAMES RIDDICK PARTINGTON.

ANHYDROUS oxalic acid is readily prepared by the following method. A mixture of 5 g. of the hydrated acid with 100 c.c. of toluene, previously distilled over calcium chloride, is distilled in a wide-necked conical flask until about 15 c.c. of liquid remain. The contents of

the flask are submitted to filtration and the solid is washed with a little dry benzene. It is then kept in a vacuum desiccator over wax for 12 hours. The product is found by titration to be pure anhydrous oxalic acid. A conical flask is used since, during distillation, the anhydrous acid separates in small needles adhering to the side of the flask which are difficult to remove from an ordinary distilling flask. The method is probably capable of application, with suitable distilling liquids, in many other cases and an attempt is being made to obtain anhydrous periodic acid in this way. A similar method using carbon tetrachloride has been described (Adams, "Organic Syntheses," 1921, Vol. I, p. 67). Since toluene has a higher boiling point than carbon tetrachloride, its use will probably expedite the dehydration.—EAST LONDON COLLEGE, UNIVERSITY OF LONDON.
[Received, May 24th, 1930.]
